



Short communication

A highly safe battery with a non-flammable triethyl-phosphate-based electrolyte



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HIGHLIGHTS

- TEP:FEC-based electrolyte enables the charge–discharge in a battery with a SiO anode.
- The electrolyte suppresses the exothermic reaction around 130 °C in a battery with a charged anode.
- The electrolyte enhances the safety of a lithium-ion battery.

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ABSTRACT

Applied in a battery with a silicon-oxide (SiO) anode, a non-flammable triethyl-phosphate (TEP)-based electrolyte with fluoroethylene carbonate (FEC) improved the safety and energy density of the battery. This TEP:FEC-based battery demonstrated almost the same performance, namely, capacity retention of 78% after 250 cycles, as that of a flammable electrolyte such as an ethylene carbonate (EC)/diethylene carbonate (DEC)-mixed electrolyte (79%). Moreover, this non-flammable electrolyte significantly enhanced the safety of the battery. This improved performance and safety is attributed to the disappearance of the exothermic peak around 120–160 °C derived from the reaction between the electrolyte and charged anode. Accordingly, this non-flammable (TEP)-based electrolyte can enhance the safety of lithium-ion batteries.

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1. Introduction

Lithium-ion batteries with high energy density and capacity for powering electric vehicles and for large-scale energy storage have been widely developed [1]. Especially, silicon as an anode and nickel oxide or cobalt oxide as a cathode are attractive materials because batteries with these materials have high capacity [2–4]. However, these batteries present safety concerns in abnormal use. For that reason, special safety technology to safeguard such high-capacity lithium-ion batteries must be developed and implemented.

To make a battery safer, non-flammable solvents have been applied as electrolytes [5]. Among those solvents, phosphate is a promising candidate owing to its non-flammability [5–12]. However, a phosphate-based electrolyte decomposes reductively on the anode, where its decomposition product deposits [13,14]. This product disturbs the reaction between lithium ions and the anode,

especially when graphite is used as an active material. Some solutions to resolve this problem, such as additives to form a film to suppress the phosphate decomposition, have been suggested [15–17]. Effective additives, however, have not yet been found.

Under the above-described circumstances, in the present study, TEP was selected as a phosphate because it has low viscosity and high solubility of lithium salt—which are desirable properties for a lithium-ion battery. Fluoroethylene carbonate (FEC) was found to be the most available additive for a TEP-based electrolyte in a cell with a SiO anode, even if TEP solvent was used as an electrolyte at high concentration. Moreover, to compare this TEP-based electrolyte with a conventional electrolyte, both were evaluated in safety tests on lithium-ion batteries.

2. Experimental

Performances of batteries with the TEP-based electrolyte and a conventional electrolyte were evaluated by using a pouch cell. All electrolytes (TEP/1-M LiPF₆, EC:DEC (3:7 by volume)/1-M LiPF₆) were purchased from Ube Industries, Ltd. FEC was purchased from

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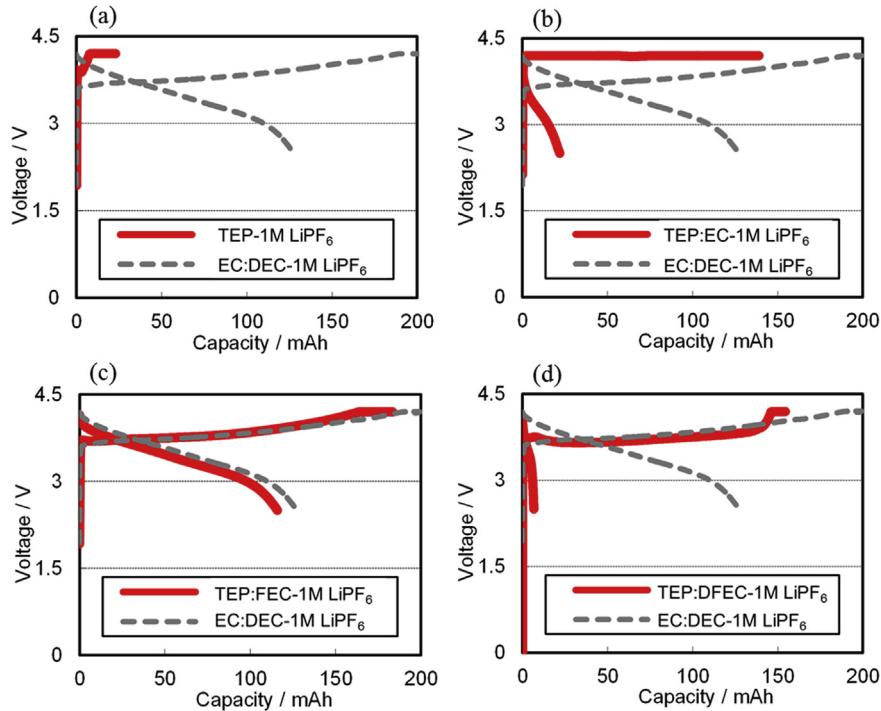


Fig. 1. First charge–discharge in TEP based electrolyte ((a)without additive and with (b) EC, (c) FEC, (d) DFEC) and EC:DEC based electrolyte.

Kishida Chemical Co., Ltd. Carbon-coated SiO powder (C–SiO) was prepared by CVD and used as an anode. C–SiO (85 wt%) and polyimide (15 wt%) were mixed in 1-methyl-2-pyrrolidone (NMP). The slurry was coated on a copper foil. The cyclo-dehydration was converted to polyimide by heating at 350 °C under nitrogen atmosphere [3]. LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ was prepared as a cathode. LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (91 wt%) powder, carbon powder (5 wt%), and polyvinylidene fluoride (PVDF) (4 wt%) were mixed in NMP and coated on aluminum foil. The anode and cathode were cut into 8.4 cm² square sheets, which were separated by a polypropylene separator and covered by laminated sheets. The pouch cells were charged at constant current (30 mA) and constant voltage (4.2 V) for a total of 12 h. They were discharged at constant current (1.8 mA (0.1C)) up to 3.0 V. The cells were evaluated by cycle tests were at 18 mA (1C rate) (total charge time: 2.5 h) instead of 0.1C. First charge–discharge and cycle test were conducted at 25 °C.

To evaluate the safety of a battery with the TEP-based electrolyte and a conventional electrolyte, the battery was subjected to an

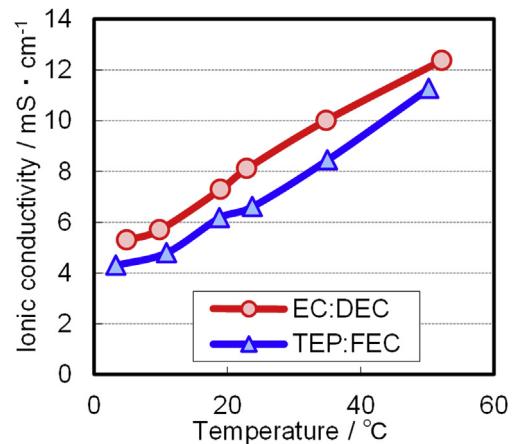


Fig. 3. Ionic conductivity in EC:DEC-based electrolyte and TEP-based electrolyte.

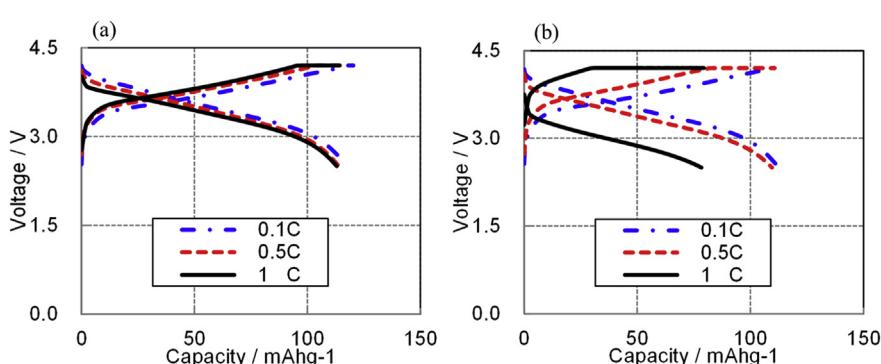


Fig. 2. First charge–discharge curve at different rate (0.1, 0.5, 1C) in (a) EC:DEC-based electrolyte and (b) TEP-based electrolyte.

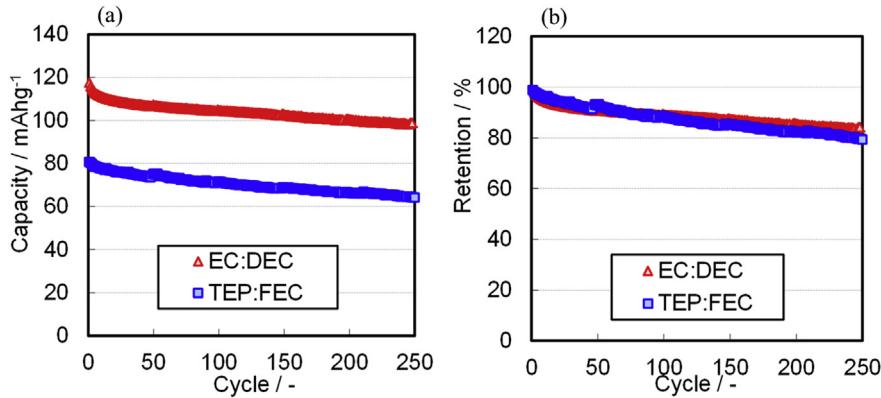


Fig. 4. Cycle performance in terms of (a) capacity and (b) retention.

external short-circuit test as follows. The TEP:FEC-based electrolyte and the EC:DEC-based electrolyte were used as electrolytes for this test. A cathode ($172 \times 84 \text{ mm}$) and an anode ($176 \times 88 \text{ mm}$) coated with each active material on both sides were prepared. Three cathodes and four anodes were stacked alternately, and each electrode was separated by a polypropylene separator. After first charge and discharge, the cell was charged up to 4.3 V at constant current (0.25 A (0.1C rate))) for 12.5 h again. 2.9 Ah as a charge capacity was obtained for both electrolyte. The cell was put in a thermostatic chamber at 55°C . The cathode and anode were connected by a $10\text{-m}\Omega$ resistor outside the cell. The surface temperature as well as the current and voltage of the cell were monitored during this test.

For differential scanning calorimetry (DSC) measurement, cells were charged at 0.1C rate up to 4.2 V (total charge time was 12 h).

Those cells were opened in a glove box. After that, the charged cathodes and charged anodes were taken out from the cells and washed in DEC solvent for a few seconds. They were cut into $3.5\text{-mm}\varphi$ pieces and used as samples for DSC measurement after adding $2 \mu\text{L}$ of electrolyte. DSC measurements were carried out at $10^\circ\text{C min}^{-1}$ from room temperature to 300°C .

3. Result and discussion

The first charge–discharge curve of the cell with a TEP-based electrolyte, when a cyclic carbonate derivative, such as EC, FEC or DFEC, was added as an additive, is shown in Fig. 1. By adding FEC, high charge–discharge capacity was obtained (Fig. 1(c)). Coulombic efficiency (64%) was high, namely, almost the same as that of an

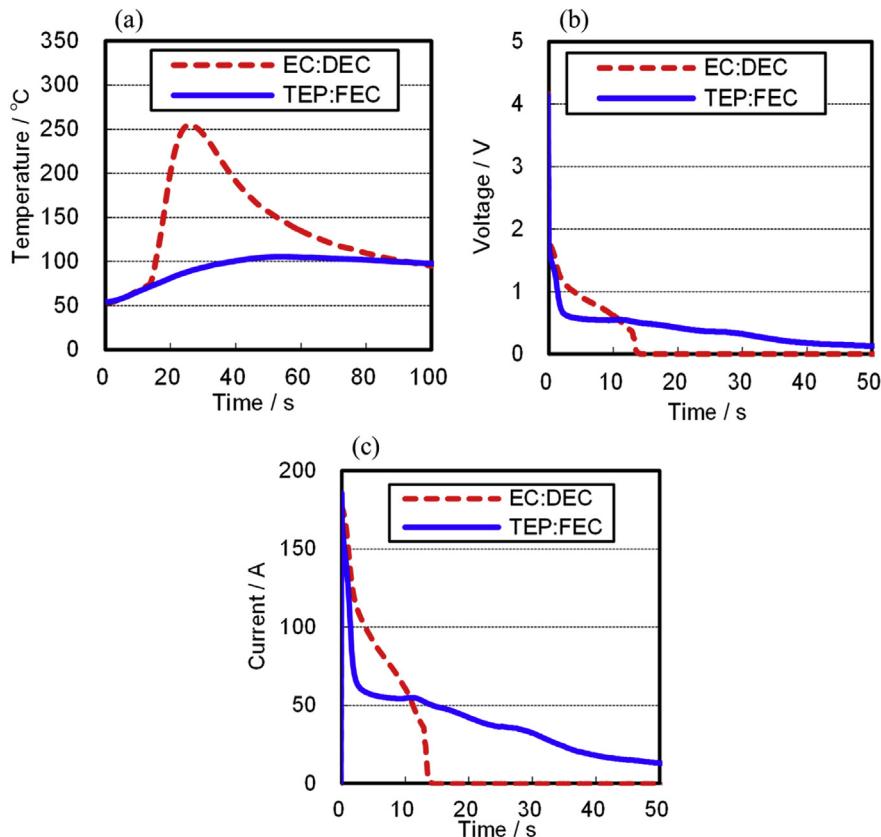


Fig. 5. (a) Surface temperature of the cell, (b) voltage, and (c) current during external short-circuit test.

EC:DEC-based electrolyte. On the other hand, as for the TEP-based electrolyte without additives, first charge–discharge capacity was low, and ethylene gas (C_2H_4) was derived from TEP decomposition on the electrode (Fig. 1(a)). This result differs from that concerning the TEP-based electrolyte with FEC. Discharge capacity was also low when EC or DFEC was used as an additive (Fig. 1(b) and (d)). EC and DFEC have similar structure to FEC, but their effects as additives were completely different. This means that FEC has a peculiar behavior in the TEP-based electrolyte. As often reported, TEP decomposes on the anode reductively. FEC was therefore suggested as a way to make a film to suppress decomposition of TEP.

The charge and discharge capacity of the TEP:FEC-based electrolyte at 1C rate was a little lower than that of the EC:DEC-based electrolyte, although the coulombic efficiency was high (Fig. 2). This is because of the lower ionic conductivity of TEP:FEC-based electrolyte, as shown in Fig. 3. Accordingly, to improve for TEP:FEC-based electrolyte, this lower-capacity issue must be addressed. However, the capacity retention of TEP:FEC-based electrolyte after 250 cycles was almost the same as that of the EC:DEC-based electrolyte (Fig. 4). This result shows that adding FEC can suppress TEP decomposition on the anode during charge–discharge cycles.

In an external short-circuit test, the cell with the TEP:FEC-based electrolyte demonstrated a higher safety compared to EC:DEC-based electrolyte. In the beginning of this test (in which the cathode and anode were externally connected by a 10-mΩ resistor), the current was highest (185 A). The surface temperature of the cell gradually increased and reached at 106 °C in 62 s. After that, the surface temperature of the cell decreased step by step. Neither fire nor gas leaks were observed in this test. On the other hand, in the case of the EC:DEC-based electrolyte, maximum current was 177 A,

which is a little lower than that of the TEP:FEC-based electrolyte. The surface temperature of the cell continued to increase during the external short-circuit test. After 16 s, the surface temperature of this cell reached around 80 °C. It then rapidly increased, and finally the cell exploded (unlike the cell with the TEP:FEC-based electrolyte). This result shows that the TEP:FEC-based electrolyte can significantly enhance the safety of a battery.

The DSC measurements for electrolytes without an electrode, with a charged anode, and with a charged cathode are plotted in Fig. 6. In the case of the TEP:FEC-based electrolyte, an endothermic peak is observed at 270 °C, which is a little higher than that in the case of EC:DEC-based electrolyte (Fig. 6(a)). In the case of both electrolytes, no exo- or endothermic peaks appear up to 200 °C. According to the DSC measurements of the electrolyte with a charged anode, in the case of the TEP:FEC-based electrolyte, no exothermic peak appears around 120–160 °C. That result differs from that in the case of the EC:DEC-based electrolyte. This exothermic peak depends on the type of electrolyte, and it is derived from the reaction between the electrolyte and charged anode because the EC:DEC-based electrolyte is stable around this temperature (Fig. 6(a) and (b)). In the case of the two electrolytes in the cell with the charged cathode, the exothermic peak areas and temperatures are not significantly different (Fig. 6(c)). The exothermic peak around 250 °C was attributed to the decomposition of active material.

The fact that the safety of a battery can be improved by using a TEP:FEC-based electrolyte instead of an EC:DEC-based electrolyte is discussed as follows. In an external short-circuit test, the surface temperature of the cell with the EC:DEC-based electrolyte rapidly increased after it reached around 80 °C. At this time, it seems that the internal temperature of this cell was more than 80 °C because of

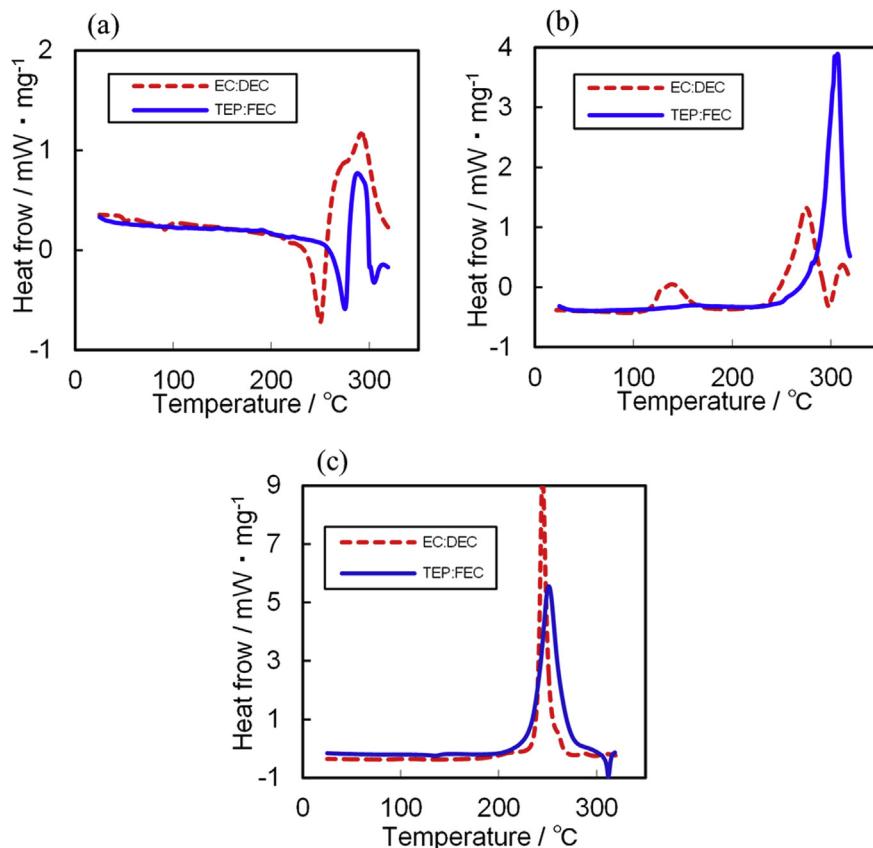


Fig. 6. DSC measurements for electrolyte (a) without electrode, (b) with charged anode, and (c) with charged cathode.

the joule heat derived from the current generated inside the cell. From the DSC measurement concerning the EC:DEC-based electrolyte with a charged anode, an exothermic peak appears after 120 °C. The heat from this exothermic reaction therefore accelerated the temperature increase inside the cell. Perhaps separator seemed to shrink due to the heat and partially internal short-circuit occurred. At the end, the temperature reached the starting temperature of thermal runaway and the cell exploded. On the other hand, in the case of the TEP:FEC-based electrolyte, no peaks appear up to 200 °C (Fig. 6(b)). From this result, we can explain about improving the safety of the cell in the external short-circuit test by using TEP:FEC based electrolyte. During this test, the surface temperature of the cell did not rapidly increase as Fig. 5(a) showed, even if it reached more than 80 °C and the internal temperature of the cell seemed to be around 120 °C. As this reason, there are no exothermic reaction with charged anode up to 200 °C in TEP:FEC based electrolyte. In other word, only the joule heat derived from the current caused to increase the temperature of the cell. After that the current decreased with time and the cell was cooled by radiating the heat from the surface. Therefore, the cell with a TEP:FEC-based electrolyte was safe up to 200 °C. These results demonstrate that the battery with a TEP:FEC-based electrolyte achieves a high safety level because no exothermic reaction occurs up to 200 °C.

4. Conclusion

FEC is an effective additive to prevent TEP decomposition in a cell with a SiO anode. That is, this additive makes it possible to use a non-flammable TEP solvent as an electrolyte. A TEP:FEC-based

electrolyte attained high capacity retention after 250 cycles. The safety of the battery with this electrolyte was markedly improved. This new non-flammable TEP:FEC-based electrolyte solvent will contribute to creating the next-generation lithium-ion battery with a high level of safety.

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